

Effect of the Microchannel Plate Design on the Capacity of Methanol Steam Reformers

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Abstract—Methanol steam reforming in microreactors is considered, and the effects of the microreactor geometry (cylindrical and rectangular) and microchannel plate (MCP) design on the hydrogen capacity of the microreactor is analyzed. The MCPs were made from aluminum foil, stainless steel, and foamed nickel by laser engraving, electrochemical etching, and pressing. The amount of catalyst powder ($\text{CuO}/\text{ZnO} = 40 : 60$ mol/mol) fixed on one MCP was 0.04–2.5 g. The specific hydrogen capacity (U_w) of the cylindrical microreactor is more than 3 times as high as the U_w of the rectangular microreactor and is 6 times as high as the U_w of a conventional fixed-bed catalytic reactor. This gain in hydrogen capacity is due to the more efficient use of the catalyst in the microreactors. The MCP design, which determines the residence time of the reactants in the microreactor, also has a significant effect on the capacity of the microreactor.

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In recent years, there has been vital interest in microchannel catalytic systems for producing hydrogen from hydrogen-containing fuels. This interest is explained by the compactness of these systems and by the fact that their catalyst is used with a higher efficiency than the catalysts in conventional catalytic systems.

Methanol is ranked among the most promising chemical substrates for obtaining hydrogen owing to its high energy content, availability, and cheapness. Catalytic steam reforming is one of the most efficient technologies for deriving hydrogen from methanol. This reaction takes place at comparatively low temperatures of 200–300°C and thus does not impose heavy demands on the construction materials of the reactor or equipment. Employing microreactors in methanol steam reforming makes it possible to create hydrogen generators for portable power sources based on fuel cells [1].

Methanol steam microreformers consist of a set of microchannel plates (MCPs) with submillimeter-sized channels. The high thermal conductivity of MCPs and the small cross-sectional area of the channels ensure high heat and mass transfer rates and a narrow reactant–catalyst contact time distribution. The design and fabrication of such microreactors involves a variety of problems, such as optimization of MCP geometry, optimization of MCP arrangement in the microreactor, and development of methods for loading and fixing the catalyst in the MCP channels.

The development of microstructured catalytic reactors was the subject of a special issue of the journal *Catalysis Today*.¹ This issue deals with various types of microreactors, kinetic and gas-dynamic phenomena in submillimeter-sized channels, and the use of these reactors in the production of hydrogen from methanol and natural gas.

There have been reports concerning the fabrication of all-metal microreactors by the diffusion welding of a stainless steel MCP stack and by tape casting [2, 3]. In the former case, the characteristic size of the channel cross section was 50–500 μm; in the latter case, 500 × 1000 and 800 × 1000 μm. The latter reactor was tested in *n*-butane oxidation on a Pd catalyst. The fabrication of a MCP from electrical silicon is described in [4]. This plate had 800 channels with a cross section size as small as 5–100 μm and, accordingly, a much larger ratio of the surface area to volume.

The autothermal oxidation of methanol was studied in two types of microreactors differing in the arrangement of gas flows in the catalytic MCPs [5]. It was found that the catalyst is most efficiently used in a cylindrical microreactor in which the gas flows not along the plates, but in the radial direction, from the microreactor center to the periphery through holes in the MCPs. This reactor with a Pd/ZnO catalyst afforded a methanol oxidation rate equivalent to a specific heat evolution rate of 425 W/(cm³ Cat).

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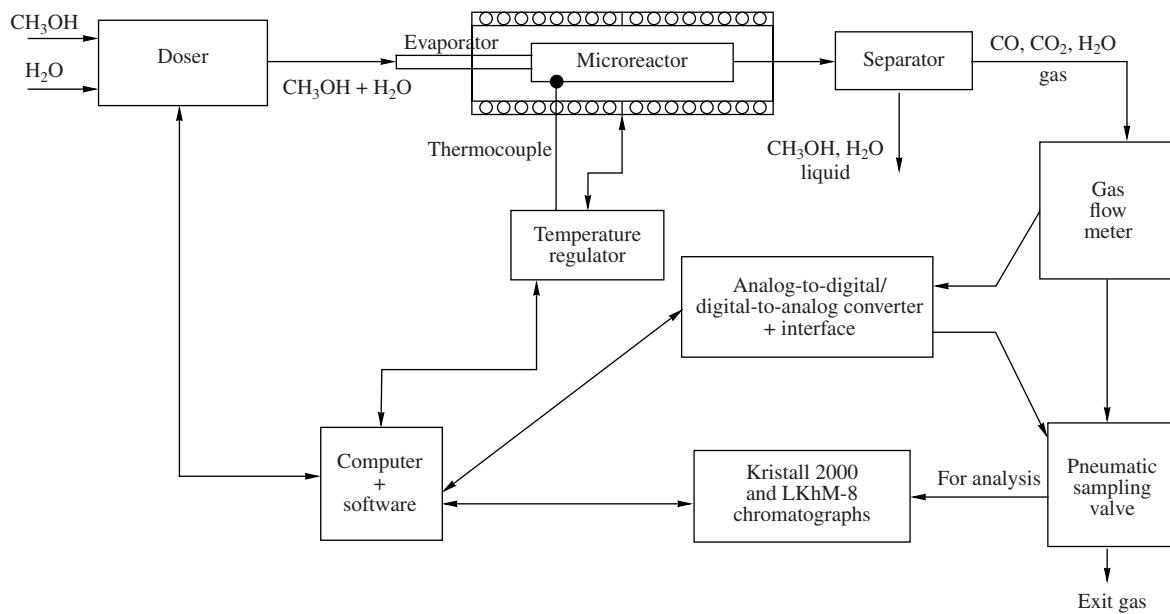


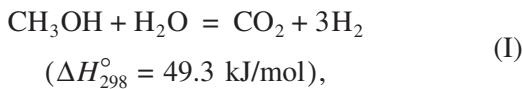
Fig. 1. Schematic of the catalytic microreactor testing setup.

Methanol steam reforming is usually carried out over rather active copper-containing catalysts having a fairly long service life. The most efficient catalysts for methanol steam reforming are the composites CuO/ZnO [6] and CuO/ZnO/ZrO₂/Al₂O₃ [7].

Here, we report the effect of the microreactor and MCP design on the catalyst efficiency in methanol steam reforming.

EXPERIMENTAL

Methanol steam reforming (MSR) is an endothermic process occurring in the presence of a catalyst at 200–300°C to yield hydrogen, as well as carbon dioxide and monoxide. Several reactions can contribute to this process. However, the linearly independent reactions are only two and they are sufficient for complete description of the material balance of the process.



Reaction (I), which is the main one, yields 3 mol of hydrogen and 1 mol of carbon dioxide per mole of methanol reacted. Reaction (II), which is the reverse of the water–gas shift reaction, yields carbon monoxide. The MSR process was carried out in the presence of a CuO/ZnO = 40 : 60 (mol/mol) catalyst with a specific surface area of ~50 m²/g. The catalyst was synthesized by a standard procedure [6, 7].

The efficiency of microreactors was tested using a catalytic setup designed at the Boreskov Institute of Catalysis, Russian Academy of Sciences, Novosibirsk.

This setup is shown in Fig. 1. The liquid dosage unit Bi-Flow (Boreskov Institute of Catalysis) allows a liquid to be fed or dosed into the reactor at a rate of 0–0.75 cm³/min with an accuracy of 5 × 10⁻⁴ cm³/min. The liquid water–methanol mixture (WMM) from the dosage unit was fed into an evaporator, which was in direct thermal contact with the microreactor. The microreactor was heated externally in a shaft furnace controlled with a MINITERM-300 temperature regulator. The microreactor temperature was measured with a chromel–alumel thermocouple welded to the microreactor body. The gas leaving the microreactor was directed to a separator, where it cooled to room temperature and the unreacted water and methanol vapors condensed. The volumetric flow rate of the leaving dry gas was measured with an AWM43300VH flow meter (Honeywell Inc.), which was calibrated on stream against a soap-bubble flow meter at intervals.

All analog signals from sensors were digitized using an ADAM 4019+ analog-to-digital converter (Advantech) and were inputted into a computer. The setup allowed the gaseous products CO₂, CO, and H₂ to be identified. This was done on a chromatographic system consisting of two chromatographs, Kristall-2000 and LKhM-8. H₂ was identified using a NaX-packed column with argon as the carrier gas, and CO and CO₂ were identified using an SKT carbon column with helium as the carrier gas. The experiments were controlled, and the results were processed using a specialized software.

The experiments were conducted as follows: The microreactor to be tested was placed into the furnace and was heated to the reaction temperature (266.7°C) in flowing argon. Next, WMM was passed through the

reactor for 2 h at a low rate. This procedure activated the catalyst. After that, measurements were taken. Blank experiments in which the catalyst was reduced in a hydrogen medium (another activation method) demonstrated that the activity of the catalyst is independent of the activation procedure: the 2-h-long reduction of the catalyst with the MSR products was equivalent to hydrogen treatment.

In MSR experiments in different types of reactors, we set the water-to-methanol molar ratio ($\beta = C_{H_2O}^{in}/C_{CH_3OH}^{in}$) and the volumetric flow rate of the liquid WMM (v_{in} , cm^3/min) fed into the evaporator. The volumetric flow rate of the dry gas mixture (v_{out} , cm^3/min), which consisted of hydrogen, carbon monoxide, and carbon dioxide, was measured at the reactor outlet, and its composition was determined chromatographically. Using the material balance equations for the elements in the feed and exit streams and knowing the carbon monoxide concentration, we were able to calculate the methanol conversion and the hydrogen yield.

The molar methanol feed rate (F , mol/min) is related to the liquid WMM feed rate as follows:

$$F = v_{in}\rho(y_{CH_3OH})/M_{CH_3OH}, \quad (1)$$

where $y_{CH_3OH} = M_{CH_3OH}/(M_{CH_3OH} + \beta M_{H_2O})$ is the methanol mole fraction in the liquid WMM feed, $M_{CH_3OH} = 32$ g/mol is the molar weight of methanol, $M_{H_2O} = 18$ g/mol is the molar weight of water, and $\rho(y_{CH_3OH})$ (g/cm³) is the WMM density. The density of a WMM as a function of its methanol content can be calculated from reference data [8]. These data can be interpolated with an accuracy of ~1% using a polynomial of degree 2:

$$\begin{aligned} \rho(y_{CH_3OH}) &= 0.9915 \\ &- 0.0943y_{CH_3OH} - 0.1033y_{CH_3OH}^2. \end{aligned} \quad (2)$$

At the same time, the volumetric flow rate of the dry gas at the reactor outlet is the sum of the flow rates of the gaseous products and is related to F as follows:

$$v_{out} = V_0F(4x - \varepsilon), \quad (3)$$

where $x = (C_{CH_3OH}^{in} - C_{CH_3OH}^{out})/C_{CH_3OH}^{in}$ is the methanol conversion, $\varepsilon = C_{CO}^{out}/C_{CH_3OH}^{in}$ is the methanol fraction converted into carbon monoxide, and $V_0 = 24.6 \times 10^3$ cm³/mol is the volume of 1 mol of an ideal gas at $T = 300$ K and $P = 1$ atm. Equations (1) and (3) lead to the following expressions for the methanol conversion

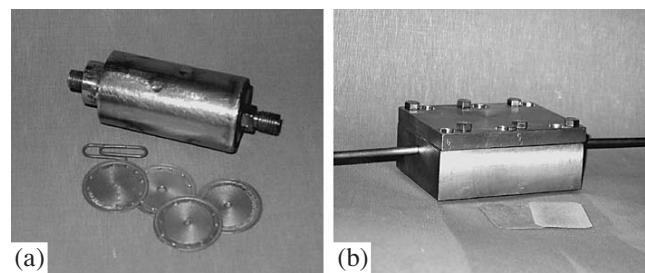


Fig. 2. Appearance of the (a) CMR and (b) RMR.

x and the hydrogen capacity U_{H_2} (cm³/min) of the reactor (or hydrogen yield):

$$x = \frac{1}{4V_0\gamma} \frac{v_{out}}{v_{in}} + \frac{\varepsilon}{4}, \quad (4)$$

$$U_{H_2} = V_0\gamma(3x - \varepsilon)v_{in}, \quad (5)$$

where $\gamma = \frac{\rho(y_{CH_3OH})y_{CH_3OH}}{M_{CH_3OH}}$ (mol/cm³) is the number of

moles of CH₃OH in 1 cm³ of the liquid WMM. It is clear from these formulas that, in order to calculate the methanol conversion and the hydrogen capacity of the reactor, it is necessary to know the liquid WMM feed rate, the volumetric flow rate of the dry gas leaving the reactor, and the carbon monoxide concentration in this gas.

We tested three types of reactors, namely, a stainless steel cylindrical microreactor (CMR, Fig. 2a), a brass rectangular microreactor (RMR, Fig. 2b), and a quartz tubular fixed-bed reactor (FBR).

In the CMR, we used two types of disc-shaped MCPs 29 mm in diameter (MCPD-1 and MCPD-2; Figs. 3a, 3b). On both sides of the MCPD-1 plates, which were made from a stainless steel sheet of thickness 0.35 mm, we produced, by electrochemical etching, randomly arranged teardrop-shaped pits of diameter ~100 μ m and depth ~50 μ m. The pit density was ~320 cm⁻² [9]. The pits were then completely filled with a catalyst containing pseudoboehmite as the binder (catalyst/binder = 70 : 30 w/w). The particle size of the catalyst was ~10 μ m. The total weight of the catalyst per MCP was 40 mg.

The MCPD-2 plates were made from aluminum and had a thickness of 250 μ m. Parallel channels with a cross section of 30 \times 50 μ m were laser-engraved on both sides of each plate so that the channel spacing was 80 μ m. The channels on one side were perpendicular to the channels on the other side. Because laser engraving was carried out in a pulsed mode, the bottom of the channel had marked roughness with a characteristic size of 20 μ m. Again, the channels were completely filled with a catalyst–binder mixture with the same composition. Note that the roughness of the channel bottom ensured good fixation of the catalyst particles

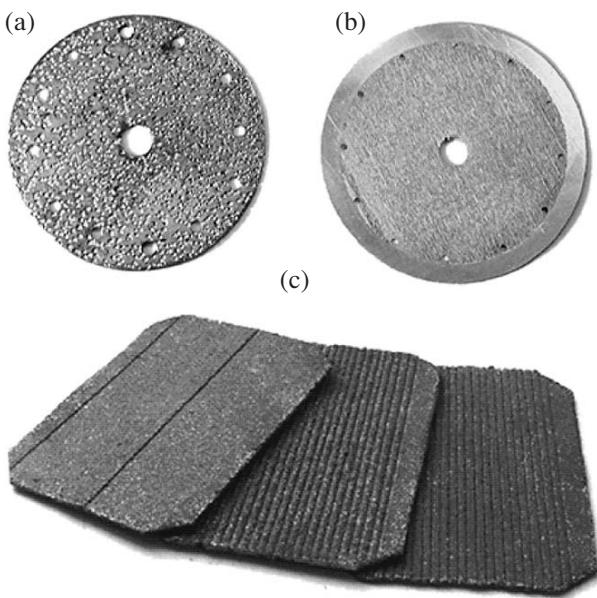


Fig. 3. Microchannel plates (a) MCPD-1, (b) MCPD-2, and (c) MCPR-5.

(~10 μm in size). The catalyst weight per MCPD-2 plate was 45 mg.

In the RMR, the MCPs (MCPR-1 through MCPR-5) were made from foamed nickel (ZAO Novomet-Perm) with the following properties: open porosity, 0.8; average size of a structural cell, 0.25 mm; specific surface area, 10 m^2/g . The catalyst was fixed on these plates as follows: An original foamed-nickel plate, 2–3 mm in thickness, was loaded with a catalyst–binder (pseudo-boehmite) powder (70 : 30 w/w) by ultrasonication in an ethanolic dispersion. The catalyst particle size was ~10 μm . After air drying, the plate was cold-pressed at 250 atm using a special-purpose die. This yielded 30 \times 40 mm plates of thickness 0.5 mm with straight channels of the desired geometry (Fig. 3b). In all cases, the weight of the pressed catalyst was determined by weighing the plate before and after the catalyst loading procedure. The following MCPs were thus made: MCPR-1, with two parallel flat channels with a cross section of 0.2 \times 10.0 mm separated by a 3.0-mm-wide barrier; MCPR-2, with 33 parallel channels with a cross section of 0.2 \times 0.2 mm separated by 0.3-mm-wide barriers; MCPR-3, with 25 channels of the same geometry separated by 0.8-mm-wide barriers; MCPR-4, with 25 parallel channels with a cross section of 0.1 \times 0.1 mm separated by 0.9-mm-wide barriers; MCPR-5, with 25 parallel channel with a cross section of 0.5 \times 0.5 mm separated by 0.5-mm-wide barriers.

The CMR was tested with ten MCPD-1 or MCPD-2 plates inside. A 0.05-mm slit between two plates was produced using a 2-mm-wide aluminum ring placed at the periphery of an MCP disc. The CRM was sealed by circular welds at its ends. In this type of microreactor, the feed flows past the MCPs in a parallel manner. From

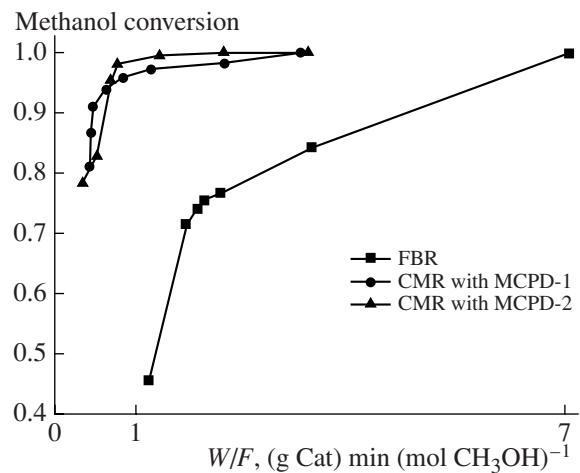


Fig. 4. CH_3OH conversion (x) as a function of W/F for the CMR with different microchannel plates and for the conventional FBR at 266.7°C.

the periphery of each disc, it moves over the disc plane in the radial direction to the center, accumulates in the axial zone, and then leaves the reactor.

In the RMR, we placed two rectangular plates (MCPR-1–MCPR-5). The reactor and the MCPs were sealed with graphite gaskets. The feed in this type of reactor flows along the MCPs.

The FBR was a quartz tube with an inner diameter of 6 mm. The tube was packed with a Cu/ZnO (40 : 60 mol/mol) catalyst with a pellet size of 0.25–0.5 mm. The total weight of the catalyst was 0.5 g.

RESULTS AND DISCUSSION

The MSR process in the microreactors was studied for a WMM consisting of 1 mol of CH_3OH and 1 mol of H_2O ($\beta = 1$), in accordance with the stoichiometry of the reaction. In view of this, Eqs. (4) and (5) reduce to

$$x = 5.7 \times 10^{-4} \frac{V_{\text{out}}}{V_{\text{in}}}, \quad (6)$$

$$U_{\text{H}_2} = 0.75 V_{\text{out}}. \quad (7)$$

As was found experimentally, the methanol fraction converted into carbon monoxide (ϵ) can be neglected since the outlet CO concentration does not exceed 5 vol %.

Figure 4 plots the observed methanol conversion x as a function of W/F (the reciprocal of the specific methanol flow rate or, in other terms, the reciprocal of the methanol molar feed rate F divided by the catalyst weight W (g)). In the CMR, no matter what the plate type, the methanol conversion of 0.8 is reached at $W/F = 0.5 \times 10^3$ (g Cat) min (mol CH_3OH)⁻¹. In the FBR, the same methanol conversion is observed at $W/F = 3 \times 10^3$ (g Cat) min (mol CH_3OH)⁻¹. Hydrogen yield data calculated as $U_{\text{H}_2} = 73.8 \times 10^3 x F$ for the

Table 1. Total catalyst weight, the reaction volumes of the FBR and CRM reactors, and the total and specific hydrogen yields for a methanol conversion of 0.8

Reactor and plate types	W , g	V^* , cm ³	$W/F \times 10^3$, g min mol ⁻¹	U_{H_2} , cm ³ min ⁻¹	U_V , cm ³ min ⁻¹ (cm ³ RV) ⁻¹	U_W , cm ³ min ⁻¹ (g Cat) ⁻¹
CMR:						
MCPD-1	0.40	2.00	0.5	46.6	23.3	116.6
MCPD-2	0.45	2.80	0.5	53.3	18.3	118.3
FBR	0.50	0.28	3.0	10.0	33.3	20.0

* V is the reaction volume (RV), which is equal to the catalyst volume.

Table 2. Total catalyst weight, reaction volume, MCP channel parameters, and the total and specific hydrogen yields at a methanol conversion of 0.8 for the RMR

Parameters	MCPR type				
	MCPR-1	MCPR-2	MCPR-3	MCPR-4	MCPR-5
Catalyst weight W , g	2.43	2.31	1.62	2.32	2.19
Channel surface area, cm ²	24.3	16.2	12.3	6.14	26.7
Channel volume, cm ³	0.320	0.094	0.070	0.018	0.350
Reaction volume, cm ³	1.31	1.52	1.80	1.54	1.62
$W/F \times 10^3$, g min mol ⁻¹	1.6	3.0	4.0	8.5	6.0
U_{H_2} , cm ³ min ⁻¹	88.0	45.0	23.3	15.0	20.0
U_V , cm ³ min ⁻¹ (cm ³ RV) ⁻¹	66.6	30.0	13.0	9.6	12.3
U_W , cm ³ min ⁻¹ (g Cat) ⁻¹	36.70	19.50	14.30	15.50	9.17

methanol conversion of 0.8 are listed in Table 1. The performance of the reactors was characterized in terms of hydrogen yield per unit reaction volume (RV), which is the unit volume occupied by the granular catalyst or the MCPs (U_V , cm³ min⁻¹ (cm³ RV)⁻¹), or in terms of hydrogen yield per unit weight of the catalyst (U_W , cm³ min⁻¹ (g Cat)⁻¹). Both characteristics are presented in Table 1. The hydrogen yield U_{H_2} is higher for the CMR than for the FBR. Therefore, at nearly equal catalyst weights in these reactors, methanol conversion is more efficient in the CMR than in the conventional tubular FBR. In other words, the catalyst is more efficiently used in the microreactor than in the conventional tubular reactor with a granular catalyst. Note that the hydrogen yield per unit reaction volume (U_V) is higher for the FBR than for the CMR. At the same time, the hydrogen yield per unit weight of the catalyst (U_W) is much higher for the CMR than for the FBR (Table 1). This difference between the specific hydrogen yield values is unambiguous evidence that the catalyst is more efficiently used in the microchannel reactor. The smaller U_V value for the CMR is due to the fact that U_V is calculated for the total MCP volume, which consists of the volume of the fixed catalyst and the volume of the microstructured support (metal plate), while the latter depends on the MCP-making technology.

Experimental data for the RMR, with the rectangular plates MCPR-1–MCPR-5, are presented in Fig. 5

and Table 2. The highest hydrogen capacity is achieved with MCPR-1 plates, which have two channels with a cross section of 0.2 × 10 mm. Let us compare the performances of the CMR and the RMR. It is clear from Tables 1 and 2 that the specific capacity U_V of the RMR with MCPR-1 plates is nearly 3 times as high as that of the CMR with MCPD-1 plates. However, the opposite situation is observed for U_W . Therefore, much of the

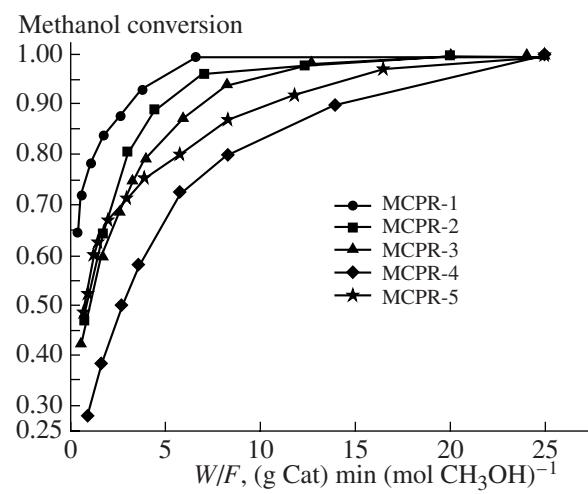


Fig. 5. CH₃OH conversion (x) as a function of W/F for the RMR with MCPR-1–MCPR-5 microchannel plates at 266.7°C.

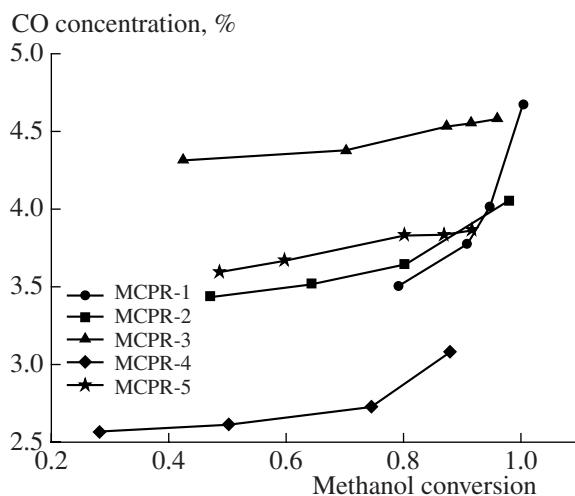


Fig. 6. CO concentration at the outlet of the CMR as a function of the CH_3OH conversion at 266.7°C.

catalyst pressed into the foamed-nickel plate MCPR-1 is used in the reaction less efficiently than the catalyst in the CMR. Consequently, in the RMR, the reaction occurs in a thin surface layer of the catalyst pressed in foamed nickel and the reaction rate is likely limited by the diffusion of the reactants across this layer. This inference is confirmed by the absence of a correlation between the hydrogen yield in the RMR and the weight of the catalyst fixed on the MCPs, as well as by the existence of a correlation between U_{H_2} and the total surface area of the channels (i.e., the catalyst-covered MCP area accessible to the reactants (Table 2)). The only exception here is MCPR-5, which has large channels with a cross section of 0.5×0.5 mm. Furthermore, this inference is indirectly confirmed by the fact that the diffusion limitations imposed on the products of reaction (I) coming out of the catalyst layer can shift the equilibrium in reaction (II) and can thus raise the CO concentration at the RMR outlet relative to the CO concentration at the CMR outlet [10]. This increase in the CO concentration was indeed observed in earlier experiments [11]. For the CMR with MCPD-2 plates, which contain a thin catalyst layer, the CO concentration is 1–1.5%. For the RMR with MCPR-1 plates and a thick layer of a fixed catalyst, the CO concentration is 3–5%.

The fact that MCPR-5, which has a rather large channel surface area as compared to the other plates, affords only a low hydrogen yield is explained by the large cross section of the channels. It was demonstrated in an earlier work [12] that increasing the channel cross section above 0.5×0.5 mm impairs mass transfer between the reactant stream and the catalyst fixed on the channel walls.

Figure 6 plots the outlet CO concentration as a function of the CH_3OH conversion for RMR with MCPR-1–MCPR-5 plates. As would be expected, the CO concentration increases with increasing methanol conversion

for all MCPs. The lowest outlet CO concentration (2.5–3.0 vol %) is observed for the RMR with MCPR-4 plates, which have the narrowest channels (0.1×0.1 mm in cross section) and afford the lowest hydrogen yield. For the other MCPs, the CO concentration is rather high (3.5–4.8 vol %) and is correlated with the hydrogen yield. The only exception in this case is MCPR-3. Additional experiments are required for a more detailed analysis of methanol steam reforming in the microchannel reactors. Such an analysis will be the subject of a forthcoming publication.

CONCLUSIONS

Our experiments have revealed some specific features of methanol steam reforming in microchannel reactors of various designs with various types of MCPs. For analysis of the catalyst use efficiency in the microchannel reactors, we tested a conventional tubular reactor with a fixed catalyst bed and microreactors with various MCPs. For the CMR, the specific hydrogen capacity on the catalyst weight basis is >3 times higher than the same parameter for the RMR and 6 times higher than the same parameter for the fixed-bed reactor. These data suggest the following inferences:

In the methanol steam reforming process, the catalyst is more efficiently used in the microchannel reactors than in the conventional fixed-bed reactor. This difference arises from the specific features of the reactors examined. For example, a fixed bed of large catalyst pellets has a lower thermal conductivity than a catalyst layer fixed on a microstructured metallic support.

The accessibility of a catalyst to the reactants is determined by the surface area and the thickness of the catalyst layer. Because of this, the MCPD-1 and MCPD-2 plates, with a 50- μm -thick catalyst layer, afford a higher specific hydrogen yield than the MCPR-1–MCPR-5 plates, with a 250- μm -thick catalyst layer. Thus, only a thin catalyst layer works efficiently in methanol steam reforming.

The hydrogen yield for the MCPR-1–MCPR-4 plates is correlated with the area accessible to the reactants and is independent of the channel cross section. The highest hydrogen yield was achieved with MCPR-1, whose channel cross section is 10.0×0.2 mm, and the lowest hydrogen yield was observed for MCPR-5, whose channel cross section is 0.5×0.5 mm. This is explained by the retardation of mass transfer between the reactants and the catalyst layer because of the large channel cross section.

The specific hydrogen yield per unit volume of the reaction zone or per unit volume of MCP is higher for the MCPR-1 plate than for the disc-shaped plates MCPD-1 and MCPD-2. This is possibly evidence that the thickness of the efficiently used catalyst layer does not exceed 250 μm .

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